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Polypropylene Composites Reinforced with Biodegraded Sugarcane Bagasse Fibers: Static and Dynamic Mechanical Properties

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The present work aimed to study sugarcane bagasse fibers pre-treated with fungi and using NaOH/anthraquinone (AQ) in chemical pulping processes for applications in composite materials. Bagasse was decayed with 250 mg of Ceriporiopsis subvermispora inoculum in a 20 L bioreactor. After that, samples were submitted to similar conditions of decaying without inoculum charge. Decayed and undecayed fibers were treated with NaOH 12.5 wt%, 0.15 of AQ and a 12:1 (v/w) liquor:bagasse ratio at 160°C. Then, all obtained fibers were characterized according to their chemical composition. Dried biotreated (decayed) and control (undecayed) fibers were mixed through an extruder process with polypropylene. Later, composite granulates were injected directly in mold with cavities for tensile, flexural and shear tests. Composite materials with 10 and 20 wt% fibers were submitted to static mechanical standard tests and DMA (Dynamic Mechanical Analysis) to evaluate the effect of biotreatment. Biotreatment, cook time (pulping), and fiber content contributed to improvements in the mechanical properties of the composites. The interface between fiber and matrix was increased with the biotreatment and pulping of fibers. Furthermore, DMA results also showed that fiber incorporation into PP improved the modulus, mainly for biotreated fibers/PP composites. The T_g (tan δ data) from composites was dislocated at lower temperatures with respect to neat PP due to the influence of fibers on matrix.

Keywords: *Biodegradation; sugarcane bagasse; Ceriporiopsis subvermispora; composites; Mechanical properties; DMA.*

Introduction

In recent years, there has been an increasing trend toward more efficient utilization of residual agroindustrial products such as sugarcane bagasse (generally known as "bagasse") [1,2]. Brazil is the largest sugarcane producer, and the total forecast of sugarcane in the 2011/12 harvest is 652.015 million tons [3] Sugarcane generates several residual agricultural products such as bagasse in alcohol and sugar production. Bagasse is the fibrous residue of sugarcane after crushing and the extraction of sugarcane juice and is one of the largest residual agriculture products in the world [4] Sugarcane bagasse is composed of three main macromolecular components: 50% cellulose, 25% polyoses and 25% lignin [5,6]. Several processes and products have been reported that utilize bagasse as a raw material. These include the production of dissolving pulp, paper pulp, ethanol and the reinforcement of polymeric matrices [1,4,5,7,8].

The natural, bio-degradable features and chemical constituents of sugarcane bagasse have been attracting attention as a highly useful and versatile ingredient in composite materials. Eco-friendly and low cost considerations have set the momentum for material science researchers to identify green materials that give low pollutant indexes [4] Vegetable fiber reinforced polymer composite materials have been increasingly accepted for use in the construction and automotive industry because they combine advantages of both the fibers and the thermoplastic matrix [9] Such advantages include low cost, good thermal and acoustical insulation properties, availability, CO_2 sequestration enhanced energy recovery, reduced dermal and respiratory irritation, and reduced tool wear in machining operations [10] Indeed, fiber incorporation into a polymer is known to cause substantial changes in the mechanical properties of composites [11] The problem with combining vegetable fibers or lignocellulosic materials with a thermoplastic is their incompatibility [12] Incompatibility has been associated with the polar nature of the fibers and the interaction with the non-polar matrix. These problems are

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usually reduced by properly modifying the interface, which can alter the fiber surface [13]. After modification, treatment of the fibers is necessary for composite production. Vegetable fibers are rich in cellulose, the biomaterial with the highest Young's modulus [14]. In this work, an initial pre-treatment with fungi was proposed, aiming to facilitate lignin and hemicellulose removal during chemical pulping, resulting in fibers with higher cellulose contents.

The use of fungi for nonwoody plants prior to chemical treatment or mechanical refining has also received attention in recent years [15-17]. *Ceriporiopsis subvermispora* is a white-rot fungi utilized in several papers involving treatment of lignocellulosic materials [8,18,19]. In addition, its influence on the rate of delignification prior to chemical pulping has been reported by various laboratories [20,21]. Biological pretreatment with white-rot-fungi increases the delignification rates and allows preparation of biopulps in shorter cooking times, resulting in energy savings or increased digester throughput [22].

During the biodegradation of bagasse, the white-rot-fungi degraded the lignin, leaving the cellulose, providing nutrients and energy for fungi. In this process, the broken lignin is most likely deposited on the fiber surface. Lignin is a hydrophobic macromolecule that is compatible with thermoplastic polymer because its structure is essentially aromatic. In addition, this work applied chemical pulping to the biotreated fibers. This alkaline process has shown to be highly suitable for pulping agroresidues, incorporating good strength properties into the thermoplastic [19].

The objective of this work was to incorporate the biotreated fiber into polypropylene (PP). The composites were obtained by an extruder process, and the adhesion between fiber and matrix was determined by static and dynamic mechanical tests. The obtained composites were characterized mechanically by tensile, flexural and shear tests. Tensile and flexural standard tests are designed to produce data for the control and specification of composites materials. These data are also useful for qualitative characterization and for research and development (ASTM D638 and ASTM D790) [23,24]. Interlaminar shear strength tested by the short-beam method (ASTM D2344) [25] is a standard test procedure widely accepted for the determination of fiber/matrix interface characteristics. The short-beam test has become one of the most popular methods used in the industry to determine the interlaminar shear bond quality of composites due to the ease of specimen preparation and the simplicity of the experimental procedure [9]. Dynamic mechanical analysis (DMA) is an effective method for studying the relaxations in polymers and thereby the behavior of the material under various conditions of stress, temperature, and types of fiber. This analysis furnished information about storage and loss moduli (associated with the T_g), and tan δ is associated with the impact resistance [26]. In addition, DMA is related to the mobility of the polymer chain segments, and it has been widely used in studies on composite materials, where a more careful approach for anisotropic materials is currently required [27].

2. Experimental

2.1 Sugarcane Bagasse

Sugarcane bagasse was provided by Usina Ester of Cosmópolis (SP, Brazil). Bagasse was air-dried to a final humidity of 10% and stored at 4°C. Bagasse fibers were measured, with an average size from 10 to 50 mm in length and a 0.4 mm diameter. These measurements were accomplished using a Mitutoyo caliper (with a resolution of 0.01 mm). The chemical composition of the bagasse was determined according item 2.5, consisting of cellulose (43.8%), polyoses (28.6%), insoluble lignin (23.5%), H_2SO_4 soluble lignin (0.2%), and ash (1.3%), as demonstrated in Table 1.

2.2 Preparation of Biotreated Fibers

2.2.1 Fungi and Inoculum Preparation

C. subvermispora (Pilat) Gilbn. & Ryv. cultures, kindly provided by Prof. M. Speranza from the Universidad de la Republica, Montevideo, UY, were maintained on 20 g/L malt-extract (OXOID Ltd., England) agar plates at 4°C. This strain (catalog number CS-1) is available at the Department of Biotechnology, Engineering School of Lorena (EEL-USP), Brazil. Two hundred mL of liquid medium containing potato extract broth (24 g/L) (DIFCO, USA) and yeast extract (7 g/L) (OXOID Ltd., England) was inoculated with 20 discs (8 mm in diameter) of *C. subvermispora*-precultured solid medium. This liquid culture was maintained unshaken for 10 days at 27°C. The grown mycelium mat was filtered and washed with 300 mL of sterile water. Mycelium obtained from several cultures was blended with 100 mL of sterile

Table 1. Chemical composition of decayed (biotreated) and undecayed (control) bagasses as well as their respective NaOH/AQ pulps (30 and 60 min) incubated for 30 days with *C. subvermispora* and compared with *in natura* bagasse.

Components (%)	*in natura bagasse*	Control bagasse	Biotreated Bagasse	Control pulps (30 min)	Biotreated pulps (30 min)	Control pulps (60 min)	Biotreated pulps (60 min)
Glucan	43.8 ± 0.2	39.8 ± 0.5	39.0 ± 0.7	58.5 ± 0.3	54 ± 0.2	54.5 ± 0.5	55.7 ± 0.5
Acetyl	2.0 ± 0.1	2.9 ± 0.1	2.2 ± 0.3	n.d	n.d	n.d	n.d
Xylan	27.1 ± 0.3	24.7 ± 0.3	23.0 ± 0.8	25.3 ± 0.2	22.5 ± 0.1	26.4 ± 0.7	23.6 ± 0.4
Arabinan	1.5 ± 0.1	1.6 ± 0.1	1.5 ± 0.1	2.0 ± 0.1	1.7 ± 0.1	2.3 ± 0.1	1.8 ± 0.1
Total Carbohydrates	74.4 ± 0.4	69 ± 0.6	65.7 ± 1.1	85.8 ± 0.4	78.2 ± 0.2	83.2 ± 0.7	81.1 ± 0.6
Klason Lignin	23.4 ± 0.5	21.7 ± 0.3	18.8 ± 1.1	5.7 ± 3.0	5.5 ± 0.2	4.4 ± 0.1	6.9 ± 0.3
Soluble Lignin	0.2 ± 0.1	2.1 ± 0.1	3.1 ± 0.4	1.7 ± 0.1	2.0 ± 0.2	2.0 ± 0.4	3.3 ± 0.1
Total Lignin	23.6 ± 0.5	23.8 ± 0.3	21.9 ± 1.2	7.4 ± 3.0	7.5 ± 0.3	6.4 ± 0.4	10.2 ± 0.3
Total Ash	1.3 ± 0.6	2.1 ± 0.1	2.5 ± 0.3	n.p	n.p	n.p	n.p
Others*	0.7 ± 0.6	3.9 ± 0.7	8.5 ± 1.7	6.8 ± 3.0	14.3 ± 0.4	10.4 ± 0.8	8.7 ± 0.7

*extractives; n.d not detected.; n.p not performed

water in three cycles of 15 s. The mycelium suspension was used to inoculate the bagasse in bioreactors.

An aliquot of 25-mL of extract was used for determination of the fungus mass (g/L) by filtration through quantitative filter paper. The retained material was dried at 60°C for 2 h and then at 105°C until constant weight, reaching 4 $g.L^{-1}$ of fungus. The aliquot of inoculum was calculated using a standard 100 g fungus mass for 1000 kg bagasse [8,28-30]. The constant mass of the obtained inoculum fungi was 0.4 g for 100 mL of suspension.

2.2.2. Bioreactor

Nine bioreactors were produced from a polypropylene vessel. The top of the vessel was sealed with a lid that was ventilated to the atmosphere through an exit tube. The perforated polypropylene floor, suspended above the bottom of the reactor, was supported by a stand. The air for the bioreactor comes from a regulated supply, passes through tubing and is sterilized with potassium permanganate and humidified with sterile water. Humidified air, passing through a membrane, was injected at the bottom of the reactor by low-pressure pumps at 23 $L.h^{-1}$ flow rate. The 20-L bioreactors had the following dimensions: 27-cm inferior diameter, 33 cm superior diameter, and 32 cm height.

2.2.3. Inoculation of the Bioreactor

Each 20 L bioreactor was loaded with 800 g sugarcane bagasse that had been immersed in water for a 12 h period and then drained. The bagasse was sterilized (121°C, 15 min) for two consecutive periods intermediated by a 24 h cooling period. After sterilization, the bagasse was inoculated with 250 mg. kg^{-1} of inoculum and stored at 27°C for 30 days. Humidified air, passing through a 0.2 µm membrane, was provided for the 20 L bioreactor throughout the biodegradation. After the biotreatment, the bioreactors were opened, and the bagasse was washed with water to remove the superficial mycelium. The decayed bagasse was air-dried. Six bioreactors were inoculated with 800 g bagasse. Three controls, referred to as undecayed bagasse, were also prepared using the same parameters as for the samples.

2.3 Soda/AQ Pulping

Pulping conditions were 9.7% of Na_2O, 0.15% AQ and a liquid:bagasse ratio 12:1 (v/w). Soda cooking was performed in a 1000 mL stainless steel reactor at 160ºC for 30 or 60 minutes. The pulps were washed, bringing the pH to 6.8, and then filtered and air dried [8].

The pulp yield was calculated using equation 1 (dry mass represents the material without humidity). In equation 1, the term *RT* is the total yield in %, *M* is the bagasse mass in g (dried base) and *m* is pulp mass after pulping (g) (dried base).

$$RT = \frac{m}{M} \times 100 \quad (1)$$

2.4 Estimation of kappa number and determination of viscosity

The kappa number of pulps was estimated using the standard methodology, Tappi T236 cm-85 [31], and the pulp viscosity was determined via the standard Tappi T230 om-94 [32] methodology.

2.5 Chemical analysis of in natura, decayed and undecayed bagasse and pulp

The modified method standardized by ASTM D 271-48 [33] was used. One-gram samples of bagasse and pulp were treated with 5 mL of 72% H_2SO_4. After 7 minutes of stirring at 45°C, 25 mL of water was added to the mixture, which was hydrolyzed under 1.05 bar pressure for 30 minutes. The product was filtered, and the insoluble portion (insoluble lignin) was quantified by weighing. The hydrolysate was acidified to pH 1-3, filtered with a Sep-Pak C18 cartridge and analyzed using high performance liquid chromatography in a Shimadzu LC10 chromatograph with an Aminex HPX-87H column at 45°C. The mobile phase was H_2SO_4 0.005 $mol.L^{-1}$ at 0.6 $mL.min^{1}$. Products were determined by refractive index and quantified by calibration curves [34,35].

Soluble lignin in the hydrolyzate was determined via UV-Spectroscopy in a 5 mL aliquot of hydrolyzate, which was adjusted to pH 12 with 6 M NaOH and diluted 10-fold. The absorbance of the solution was read at 280 nm. The concentration of soluble lignin was determined using equation 2:

$$C_{lig} = 4.187 \times 10^{-2} \times \left(A_{lig}\,280 - A_{pd}\,280 \right) - 3.279 \times 10^{-4} \quad (2)$$

where C_{lig} is the lignin concentration in $g.L^{-1}$, A_{lig} 280 is the lignin solution absorption in 280 nm, and A_{pd} 280 is the absorption at 280 nm from sugar decomposition products (furfuraldehyde and hydroxymethylfurfural).

The ashes were determined with an approximately 1-g sample of bagasse and insoluble lignin. The samples with known moisture content were weighed to within 0.1 mg in a porcelain crucible that was previously calcined and weighed. The material was first calcined at 300°C and then for more than 2 h at 800°C. After calcination, the crucible was cooled in a desiccator and the mass of ash was determined by weight difference. The ash content was calculated from equation 3. In the equation, C_{zy} is the percentage of ash expressed as a percent, M_1 is the calcined mass of the empty crucible in g, M_2 is the mass of the crucible and ash in g, and M_3 is the mass of the dry straw or lignin in g.

$$C_{zy} = \left[\frac{\left(M_1 - M_2 \right)}{M_3} \right] \times 100 \quad (3)$$

2.6 Preparation of Composites

The control and biotreated milled pulp fibers of bagasse and *in natura* bagasse were dried in an oven at 80°C for 2 h. The fibers were pre-mixed with polypropylene pellets in a hopper on a forced feed system before entering the extruder screw. Fibers and PP were added to the screw rotor at 35 rpm. The temperature settings for the four temperature control zones of the extruder were as follows: zone 1 = 200°C, zone 2 = 195°C, zone 3 = 190°C, and zone 4 = 190°C. Zone 1 was the nearest to the die assembly, and zone 4 was the nearest to the hopper. The fiber/PP composites in pellets were also molded by injection using the following temperature profile: zone 1 = 200°C, zone 2 = 195°C and zone 3 = 190°C (Jasot 300/130 ton). Specimens were injected and molded at specific dimensions for tensile, flexural and shear mechanical tests.

2.7 Mechanical Tests

Composites were analyzed in an "Instron" universal-testing machine (model 4301) equipped with pneumatic claws. For tensile tests, five specimens of composites were analyzed, with dimensions in agreement with the ASTM D 638 standard [23]: 19 mm width, 165 mm length and 3.2 mm thickness at 2 $mm.min^{-1}$ cross-head speed. For flexure tests, a load was applied on the specimen at 1.3 $mm.min^{-1}$ cross-head motion rate. The 5 specimens were analyzed with dimensions in agreement with the ASTM D 790 standard [24] : 25 mm width, 76 mm length and 3.2 mm thickness. The 4-point at ¼ points flexural analysis method was used. In shear standard tests, the cross-head motion was 1.3 $mm.min^{-1}$. Specimen dimensions were 3.2 mm thickness, 19.2 mm length and 6.5 mm width according to ASTM D 2344 standard [25]

2.8 Dynamic Mechanical Analysis

Rectangular specimens having 60 x 13 x 3 mm size were used for the dynamic mechanical experiments. A dynamic mechanical thermal analyzer from TA 2100 (TA Instruments and DMA-93 accessory) was used for evaluation of dynamic moduli (storage and loss moduli) and mechanical damping (tan δ). The temperature range over which properties were measured was from -50 to 150°C at a 3°C min^{-1} heating rate with N_2 atmosphere. Two to three specimens were analyzed for each sample and then the tests were carried out at 1 Hz frequency.

3. Results and Discussion

3.1. Chemical Characterization

The sugarcane bagasse used as substrate for the biodegradation processes and later in the pulping studies was characterized for the chemical composition, and the results are given in Table 1. The Table 1 shows chemical composition differences between the control and *in natura* sugarcane bagasses. These differences can be due to the sugars and extractive the extraction during autoclave sterilization in autoclave of the control bagasse. Moreover, the Table 1 shows an 11% reduction in the xylan content for pulps obtained from biodegraded bagasse in relation to those obtained from the control bagasse and also a 32.5% increase in soluble lignin content.

The biodegradation of the lignocellulosic materials for white-rot fungi caused a certain softening of the material that can facilitate the subsequent pulping processes. On the other hand, the benefits of the pulping are not proportional to the extension of the biodelignification or the biological removal of some components from the material [36] . Further, the pulps from control and biotreated bagasses presented higher content of cellulose value, approximately 34 and 47% higher than those of *in natura* and control bagasses, respectively.

3. 1.1 Pulps characteristic

Table 2 shows the values of yield, viscosity, and kappa number for the pulps obtained from decayed sample and control medium. The Kappa number is an indication of the residual lignin content. Reduction in kappa number is lower at the beginning of pulping. By increasing cooking time, the difference in kappa number became higher. In particular, the viscosity values are low because the obtained pulp has a great amount of residue and, consequently, lignin. The viscosity values varied from 3.7-5.1 cP.

3.2. Composites Characterization

3.2.1. Static Mechanical Strength

Polypropylene composites reinforced with cellulosic fibers (pulps) from sugarcane bagasse decayed by white-hot fungi were created using 10 and 20 wt% fibers. The fibers were submitted to NaOH/AQ pulping for 30 and 60 minutes. Moreover, control pulps were also obtained for fibers undecayed with white-hot fungi. Figure 1 shows the composite systems with biotreated and undecayed (control) fibers. The specimens exhibited similar colors and shapes for different composites. Differences were observed for fibers only prior to mixing. These differences can be attributed to the quinones and chromoforus from decomposition products of lignin and carbohydrates during the biotreatment [8]. Composites reinforced with 10 wt% fibers were clearer due to their low fiber content.

Table 3 shows the results of tensile, flexural, and shear strength of polypropylene composites reinforced with biotreated fibers in respect to composites reinforced with control fibers (undecayed). The tensile strength of all composites was lower than that for neat PP and overall, and the strength decreased with the increase of added fibers. Biotreated pulps (60 min) 10 wt%/PP system was the more resistant composite material.

Natural fibers are particularly suitable for plastics reinforcement due to their high strength and stiffness. However, for the tested composites, the tensile behavior was negatively influenced by fiber insertion resulting in low strength values in respect to neat PP. An exception occurs for composites reinforced with pulps obtained after 60 min pulping: the strength tensile is similar to that of neat PP.

Flexural results showed that the properties of all composites increased in respect to neat PP, reaching 24.4% for composites with 10 wt% fiber and 37% for the composites

Table 2. Results of soda/AQ pulping of undecayed (control) sugar cane bagasse with cooking time ranging from 30 to 60 min.

Cooking Time (min)	Pulp characteristic			
	Yield (%)	Kappa number	Viscosity (cP)	Viscosity / kappa
Control pulp (30 min)	56 ± 0.4	26.0 ± 0.6	3.7 ± 0.1	0.14
Biotreated pulp (30 min)	52 ± 0.9	24.0 ± 0.6	5.1 ± 0.1	0.21
Control pulp (60 min)	51 ± 0.4	23.2 ± 0.3	5.3 ± 0.1	0.23
Biotreated pulp (60 min)	48 ± 2.0	19.3 ± 0.6	5.0 ± 0.1	0.26

Table 3. Mechanical strength of fibers/PP composites (biotreated and control sugar cane bagasse fibers).

Fibers*/PP composites	Tensile (MPa)	Flexural (MPa)	Shear (MPa)
Neat PP	27.0 ± 1.0	25.4 ± 1.0	7.2 ± 0.3
in natura bagasse 10%	23.3 ± 0.6	32.8 ± 0.4	8.2 ± 0.2
in natura Bagasse 20%	24.2 ± 1.1	31.6 ± 0.5	7.5 ± 0.0
Control pulp (30 min) 10%	24.8 ± 0.4	31.3 ± 0.2	8.4 ± 0.5
Control pulp (30 min) 20%	21.6 ± 0.7	34.2 ± 0.4	8.2 ± 0.3
Biotreated pulp (30 min) 10%	24.5 ± 0.1	31.0 ± 0.2	8.4 ± 0.2
Biotreated pulp (30 min) 20%	21.5 ± 0.2	34.0 ± 0.3	7.9 ± 0.1
Control pulp (60 min) 10%	27.0 ± 0.4	31.6 ± 0.3	8.3 ± 0.2
Control pulp (60 min) 20%	23.9 ± 0.8	34.8 ± 0.5	6.5 ± 0.1
Biotreated pulp (60 min) 10%	27.5 ± 0.9	29.4 ± 0.5	7.4 ± 0.1
Biotreated pulp (60 min) 20%	26.1 ± 0.4	32.4 ± 0.5	6.9 ± 0.2

(*) wt% reinforcement.

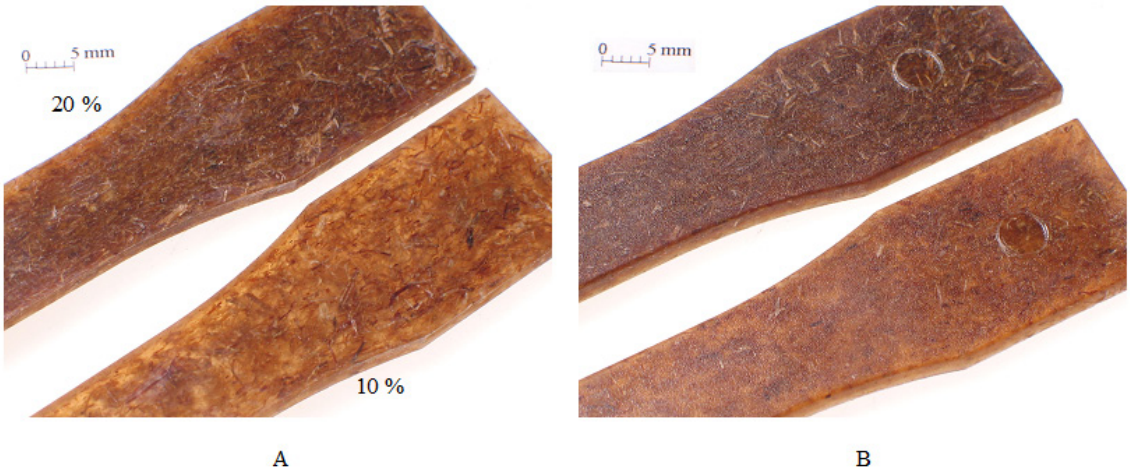

Fig 1. Polypropylene composites reinforced with pulp fibers (60 min) from biotreated bagasse obtained: a) tensile specimens of undecayed fibers/PP with 10 and 20 wt%; b) tensile specimens of biotreated fibers/PP with 10 and 20 wt%.

containing 20 wt%. However, a little increase of flexural strength value is observed for composites reinforced with decayed and undecayed fibers (20 wt%) in respect to *in natura* bagasse.

Interlaminar shear strength increased 17% in respect to neat PP for some composites reinforced with *in natura* bagasse, control and biotreated pulps (30 min) with 10 and 20 wt% fiber; and pulp (60 min) reinforced with 10 wt%. Hence, the composites reinforced with pulps are more resistant to interlaminar shear because they better disaggregate the fibers due to the pulping process.

Initially, the biodegraded fibers contain surface lignin due to the biodegradation process. However, after the pulping, the residual lignin was most likely removed from the bagasse fibers (control or biodegraded). Overall, the lignin removal and cooking time cannot significantly improve the mechanical strength.

3.2.2. Static Mechanical Modulus

The elastic modulus of materials represents the material rigidity. For this reason, the composite moduli were more rigid than that of neat PP. The elastic modulus of natural fibers like wood is approximately 10 GPa, and cellulose fiber with moduli up to 40 GPa can be separated from wood by a chemical pulping process. Such fibers can be further subdivided by hydrolysis followed by mechanical microfibrils with an elastic modulus of 70 GPa [14] . Similar to wood, bagasse can also be treated by a chemical pulping process resulting in fibers with higher moduli in respect to *in natura* fiber. Because of that, the fiber modulus enhanced the composite's properties.

Figure 2 shows the tensile and flexural elastic modulus for polypropylene reinforced with biotreated or control fibers (submitted to a NaOH/AQ pulping process for 30 or 60 min). The tensile elastic modulus of composites reinforced with various biotreated and undecayed fibers exhibited values higher than those of the neat PP, ranging from 11.2 to 58.9%. For composites reinforced with 10 wt% fibers, the modulus was higher for biotreated fibers after 60 min pulping. This also occurred among composites reinforced with 20 wt% fibers. The main reason for the modulus improvement can be related to the high disaggregation of fibers with elevated elastic modulus. Flexural modulus behavior of composites reinforced with 10 and 20% wt.

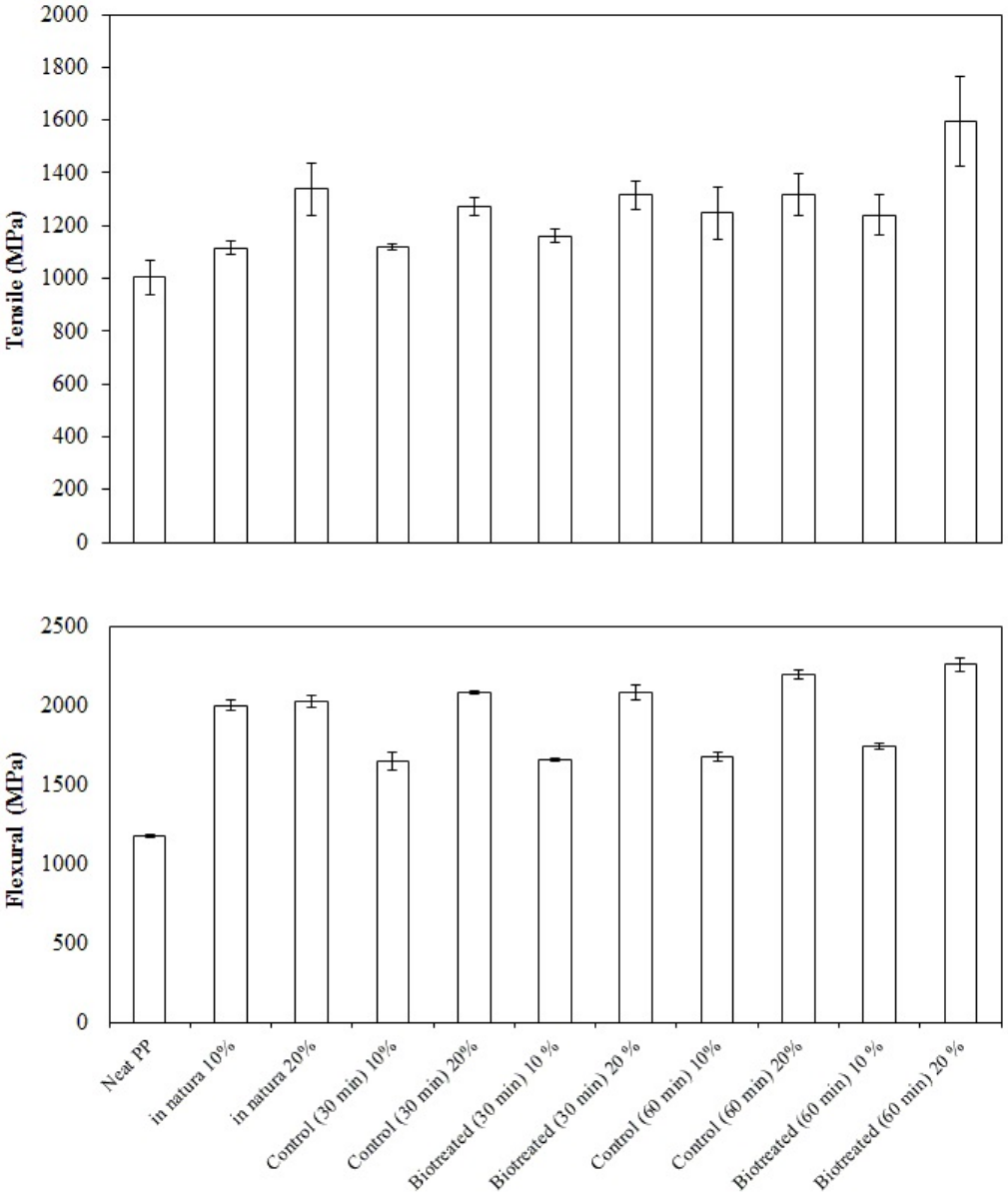

Fig 2. Tensile and flexural moduli of polypropylene composites reinforced with *in natura* bagasse, control and biotreated bagasse pulps and neat PP. Percentage of reinforcement (%) is described in weight.

biotreated and control fibers (60 min) presented better results than that of other fibers, reaching a 48.2 and 92.5% increase for pulps biotreated with 10 and 20 wt% fiber, respectively, in relation to neat PP. As a conclusion, these results show that the fiber content, biotreatment and time cooking for pulping contributed to improve the mechanical modulus, obtaining rigid composite materials.

3.2.3. Dynamic Mechanical Properties

It is well known that the physical and mechanical properties of polymeric material are strongly dependent on its structure, morphology, and relaxation process. Furthermore, the properties of composite materials are determined by the characteristics of the polymer matrices, together with reinforcements, and the adhesion fiber/matrix interface that mainly depends on the bonding strength at the interface [37]. Table 3 gives the data found in the DMA curves from neat PP and composites reinforced with decayed and undecayed bagasse pulps (30 min) and *in natura* bagasse. The storage modulus and tan δ of studied composites at -25°C (point below T_g), 25°C and the reached maximum point are reported. The glass transition temperature (T_g) and the tan δ values at T_g peak (first maximum tan δ) are also reported in Table 4.

The storage modulus values at -25°C is very close to the maximum E´. The results show that below T_g, the storage modulus raised 56.2% for decayed bagasse pulp/PP with respect to neat PP. At 25°C, the E´ decreased with respect to -25°C, but the decayed bagasse still contributed to elevated values compared to other composites.

Table 4 shows that the addition of fibers to the matrix contributed to decreasing glass transitions (T_g) of PP. Similar behavior was also observed by [37] in a study of PP reinforced with PET and PA fibers. These results have been attributed to other mechanisms of energy dissipation, such as the effects of sliding fiber/fiber that could exceed those produced by fiber/matrix interactions.

The effect of different fiber inserts (bagasse, undecayed and decayed pulps from bagasse) on the mechanical properties of PP, the storage modulus (E´) and tan δ as a function of temperature is graphically represented in Figure 3 and 4, respectively.

The Figure 3 exhibits the behavior of DMA curves for neat PP and composites. There is little change in the storage modulus between the initial temperature and 8°C for neat PP; however, for composites, the storage modulus decreases up to -25°C.

The addition of fibers contributed to increasing the modulus below the T_g and after the T_g with respect to neat PP. A higher modulus causes a small deformation on higher tension [38]. A storage modulus below the T_g is a state where the material presents elastic behavior; at temperatures around the T_g, the storage modulus decreased. The E´ and damping factor reflect the internal mobility of molecules. The fibers constrained the mobility of polymeric chains because the presence of fibers increased the storage modulus. With respect to neat PP, the storage modulus in composites increased to 56.2% (composite reinforced with 10 wt% of decayed fibers). The fungi treatment of fibers resulted in composites with better dynamical mechanical properties.

According to [39], the damping factor of composites in the transition region is governed by (1) mechanical relaxation of the matrix and the loaded fiber, (2) the interface between fiber and matrix, and (3) the fiber loading and fiber length. At temperatures around T_g of the matrix, the molecular chain has a high flexibility and the damping of the composite is primarily due to the matrix.

The damping behavior (tan δ) for neat PP and decayed and undecayed/PP and in natura bagasse/PP composites can be observed in Figure 4. The first peak from PP appears at temperatures higher than those of the composites. The insertion of fibers contributed to T_g displacement at low temperature. In this case, the addition of fibers decreased the damping values due to difficulty of polymeric chains mobility.

Table 4. Dynamic mechanical properties of polypropylene composites reinforced with 10 wt% of fibers with respect to neat PP.

Properties	PP	*in natura* bagasse/PP	Undecayed bagasse/PP	Decayed bagasse/PP
E´(GPa) at -25°C	1.49	2.07	2.26	2.33
tan δ at -25°C	0.029	0.040	0.042	0.039
E´(GPa) at 25°C	1.30	1.57	1.72	1.74
tan δ at 25°C	0.078	0.089	0.085	0.081
$E´_{max}$ (GPa)	1.50	2.07	2.28	2.35
Tg (°C)/ $\tan \delta_{max}$ *	36.0/0.088	30.5/0.093	32/0.089	31.5/0.085

*point at first relaxation peak.

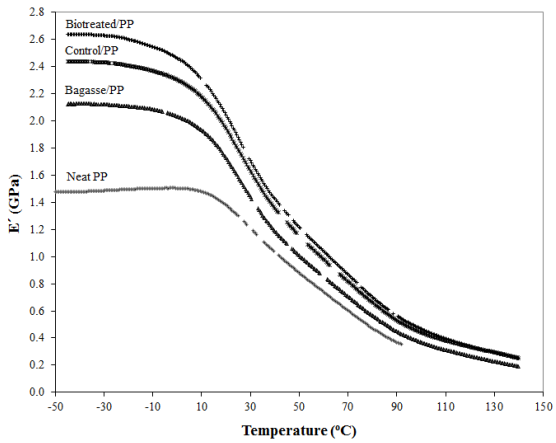

Fig 3. Storage modulus (E´) from PP composites reinforced with undecayed (control), decayed (biotreated) and *in natura* bagasses compared to neat PP.

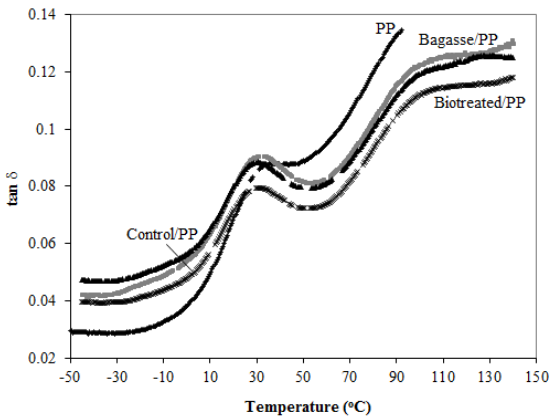

Fig 4. Tan δ curves from PP composites reinforced with undecayed, decayed and *in natura* bagasses compared to neat PP.

4. Conclusions

This work proposed the biotreatment of fibers aiming at direct application for composite materials. Pre-treatment with fungi permitted easy removal of other components from sugarcane bagasse by a pulping process with cellulose preservation. These cellulose-rich fibers resulted in better static and mechanical properties for composite material. The biotreatment, cook time (pulping), and fiber content improved some mechanical properties. The tensile strength is not influenced; however, flexure and shear strength and elastic modulus (static and dynamic) were positively affected. The interface between fiber and matrix was increased due to the biotreatment and pulping of fibers. Generally, DMA results also verify that the incorporation of fibers into PP improves moduli, mainly for biotreated fibers/PP composites. The T_g from tan δ data was dislocated at lower temperatures due to the influence of fibers on the matrix. These results permit the conclusion that the treatment of fibers by fungi and pulping processes improves the mechanical properties of final composites. These materials can be applied for various industrial components.

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